論 文 の 内 容 の 要 旨

Anhydrous Proton Conductivity of Imidazolium Hydrogen Dicarboxylates
（イミダゾールージカルボン酸塩の無水プロトン伝導性に関する研究）

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Chapter 1. General Introduction

Proton migration plays an important role in solid materials, and thus have attracted much attention not only in fundamental sciences such as quantum diffusion or proton tunneling but also in potential applications of proton conductors for electrolytes in fuel cells. [1] In particular, a lot of researches have been focused on developments of highly proton conducting materials and elucidation of the conduction mechanism. Among many proton conductors reported so far, most of them are hydrous systems performing under humidified conditions. However, such hydrous proton conductors lose conductivity above 100 °C due to desorption of water molecules. Consequently, anhydrous proton conductors are important materials in terms of not only developments of solid electrolytes above 100 °C but also scientific studies of the conduction mechanism mediated not by water molecules.

Among the anhydrous proton conducting materials, organic materials are expected to not only exhibit peculiar conductivity related to their unique assembled structures, but also enable us to systematically investigate conduction mechanism for developments of high performance materials by utilizing the rich designability of organic materials. However, there have been few reports about anhydrous organic proton conductors. As one of anhydrous organic proton conductors, imidazolium hydrogen dicarboxylates (Fig. 1) have been reported so far. [2−5] Despite the fact that no water molecules are included, these acid−base co-crystals show relatively high proton conductivity ($\sigma \sim 10^{-7}$−10^{-3} S cm^{-1}) in the form of compressed pellets. [3, 4] However, origins and mechanism of the proton conductivity has not been fully revealed due to the lack of single-crystal studies.

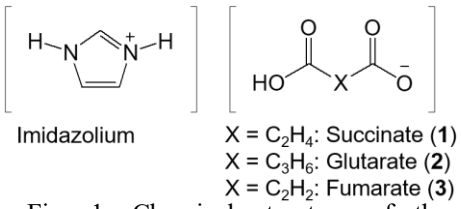

Fig. 1. Chemical structure of the imidazolium hydrogen dicarboxylates

In this study, the effects of arrangements, proton donating abilities, and dynamics of constituent molecules on the proton conductivity were investigated using high-quality single crystals of a series of the imidazolium hydrogen dicarboxylates. This study of anhydrous proton conductivity provides crucial insights into the conduction mechanism and the material design principle for the high performance anhydrous organic proton conductors.

Chapter 2. Intrinsic Proton Conductivity and its Anisotropy Reflecting "Static" Molecular Arrangements and H-bond Manners

Imidazolium hydrogen succinate (**1**), which has an unique two-dimensional (2D) H-bond network

structure [Fig. 2(a)], [2] was reported to show highest proton conductivity σ among the imidazolium hydrogen dicarboxylates. [4] In this study, in order to investigate origins of the high σ, proton conductivity measurements using the prepared single crystals [Fig. 2(b)] were performed.

As a result, the intrinsic proton conductivity without contributions from the grain boundaries was successfully observed [Fig. 2(c)]. [6] As shown in Fig. 2(c), σ along the *intra* directions [*intra A* (orange circles) and *intra B* (blue circles)] parallel to the H-bond network [Fig. 2(a)] showed much higher values than *inter* one (black circles) perpendicular to the network, which indicates that the proton conduction occurs more readily in the H-bond network than in its perpendicular direction. Additionally, σ in the *intra A* direction was higher than that in the *intra B* although the both directions are parallel to the 2D H-bond network. The *intra A* direction has only H-bonds between the acid (succinic acid) and base (imidazole) molecules, "acid–base H-bonds" [red dashed lines in Fig. 2(a)], whereas the *intra B* direction has not only acid–base H-bonds but also H-bonds between the acid molecules ["acid–acid H-bonds", black dashed lines in Fig. 2(a)]. The previous quantum dynamics simulation study by Hori *et al.* [7] suggested the faster proton transfer rates in the acid–base H-bond than that in the acid–acid H-bond, which is consistent with the observed anisotropy of σ in the H-bond network.

Therefore, the anisotropic proton conductivity measurements using single crystals demonstrated that the H-bond manners and molecular arrangements are ones of the important "static" factors realizing the anhydrous proton conduction in the imidazolium hydrogen dicarboxylates. [6]

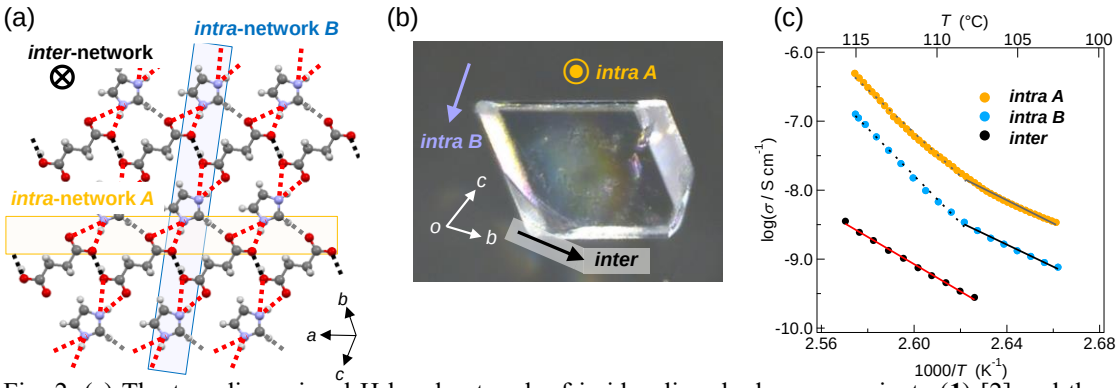

Fig. 2. (a) The two-dimensional H-bond network of imidazolium hydrogen succinate (**1**) [2] and three measured directions. (b) The relationship between the crystal shape and crystallographic axes. (c) Arrhenius plots of the proton conductivity (σ): the *intra*-network *A* (orange circles), *intra B* (blue circles), and *inter* directions (black circles).

Chapter 3. Effects of Proton Donating Abilities (pK_a) of Constituent Molecules on Anhydrous Proton Conductivity

In addition to the effect of the H-bond network structures, effects of the proton-donating abilities (pK_a) of the constituent molecules were investigated based on comparison of the σ within the H-bond networks of **1** and its analogues, imidazolium hydrogen glutarate (**2**), [3] and fumarate (**3**). [2]

As shown in Fig. 3, **1** shows more than one order higher σ than **3** at 105 °C. In addition, **2** shows 2−3 orders higher conductivity than **1** at the close temperature range. Here, the salts showing the higher

σ has smaller difference of pK_a (ΔpK_a) between the acid molecules and conjugated acid of imidazole. [8] This indicates that the smaller ΔpK_a values contributes to the higher σ, which is supported by the σ-ΔpK_a trend. [9] The smaller ΔpK_a is considered to make the barrier of proton transfer between the acid and base lower, promoting proton transport.

As a result, the proton donating ability of dicarboxylic acids is turned to be a key factor for tuning the proton conductivity of these salts, that is, small ΔpK_a between constituent acid and base molecules is one of the important "static" factors to achieve the anhydrous proton conductivity.

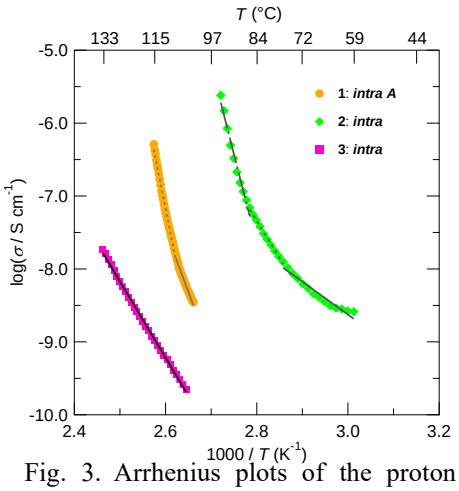

Fig. 3. Arrhenius plots of the proton conductivity (σ) for single crystals of **1** (orange circles), **2** (green diamonds), and **3** (pink squares) measured along the *intra*-network directions.

Chapter 4. Effects of Molecular "Dynamics" on Anhydrous Proton Conductivity

Interestingly, the difference of σ between **1** and **3** was expanded to more than two orders at 115 °C as shown in Fig. 3, which is attributed to non-linear dependence on the reciprocal temperature of **1** in contrast to linear dependence in **3**. The peculiar temperature dependences probably originate from the molecular dynamics, for example in libration motion of imidazolium cation observed in the previous solid-state ^{2}H NMR for **1**. [5] Then, effects of the molecular dynamics were investigated based on high-temperature structure analyses for **1** and the solid-state ^{2}H NMR for **2** and **3**.

The X-ray structure analyses on **1** at high temperature revealed that imidazolium cations in the crystal of **1** showed order-disorder transition around 80 °C. At 103 °C, a half of imidazolium cations showed orientational disordering [Fig. 4(a)], which indicates activation of the libration motion of

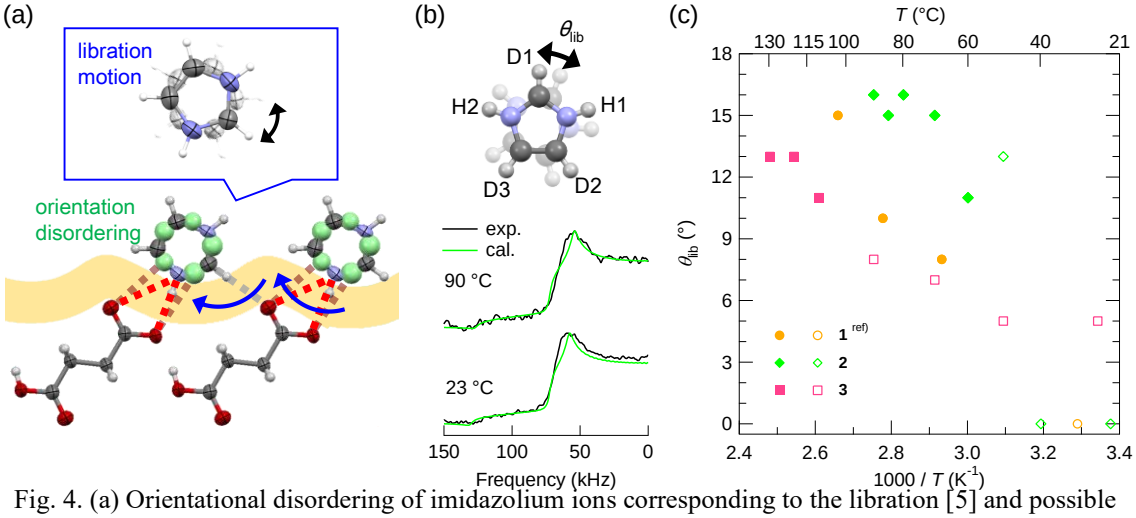

Fig. 4. (a) Orientational disordering of imidazolium ions corresponding to the libration [5] and possible conduction path along the *intra A* direction (orange belt) in **1**. (b) (upper) Schematic image of two-site jump model assuming the libration of imidazolium-d_3 molecule, and (lower) ^{2}H NMR wide-line spectra for **2** at 23 and 90 °C. (c) Libration angle θ_{lib} vs. 1000/T plots for **1** (orange circles) [5], **2** (green diamonds), and **3** (pink squares).

imidazolium cations. The imidazolium libration was expected to promote proton conduction in **1**, which is supported by a significant increase of σ along the *intra A* direction above 80 °C.

On the other hand, **2** and **3** did not show such significant changes in molecular arrangements and dynamics in the structure analyses. Thus, local imidazolium dynamics was investigated for **2** and **3** by solid-state ^{2}H NMR measurements and its simulation analyses [5] [Fig. 4(b) (the result for **2)**]. The observed imidazolium libration in **2** is considered to be significantly activated above 50 °C which is close to the starting temperature of the observation of proton conductivity around 59 °C. On the other hand, although the libration in **3** is considered to be activated already at room-temperature, as shown in Fig. 4(b), the degree of increase of the libration angle θ_{lib} in **3** is smaller than that in **2**. Moreover, the order of the magnitude of θ_{lib} values was **2** > **1** [5] > **3** [Fig. 4(c)]. This relationship of θ_{lib} is consistent with that of σ in the H-bond networks (Fig. 3). This clear correlation between σ and θ_{lib} indicates that the libration motion of imidazolium cations promotes anhydrous proton conduction in imidazolium hydrogen dicarboxylates.

Chapter 5. General Conclusion

In order to investigate the intrinsic proton conductivity and its relationship with arrangements and proton donating abilities of constituent molecules in purely organic proton conductors, imidazolium hydrogen dicarboxylates, the proton-conductivity measurements using single crystals of the three salts [(**1**) succinate, (**2**) glutarate, and (**3**) fumarate salts] were performed. [6] In addition, the effects of molecular dynamics on the anhydrous proton conductivity were investigated based on the high-temperature X-ray structure analyses and the solid-state ^{2}H NMR experiments. The results revealed the intrinsic proton conductivity of **1**−**3**, and that the H-bond network structures, small ΔpK_a between constituent acid and base molecules, and the libration motion of imidazolium molecules are the key factors for the anhydrous proton conductivity of the imidazolium hydrogen dicarboxylates.

This study demonstrates that both of the "static" factors (H-bond network structures and proton-donating abilities) and the "dynamics" of organic molecules synergistically play important roles in the anhydrous proton conduction, and thus provides crucial insights into conduction mechanism and novel material design of highly proton conductive anhydrous organic crystals.

Reference

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